TREATMENT OF COPPER-PLATING AND ZINC-PLATING WASTEWATERS FROM AN AUTOMOBILE INDUSTRY BY IRON OXIDE-COATED SAND

by

SAMIR BAJPAI

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DEPARTMENT OF CIVIL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

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TREATMENT OF COPPER-PLATING AND ZINC-PLATING WASTEWATERS FROM AN AUTOMOBILE INDUSTRY BY IRON OXIDE-COATED SAND

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by

SAMIR BAJPAI

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CERTIFICATE

This is to certify that the work contained in the thesis entitled **'Treatment of Copper-Plating and Zinc-Plating Wastewaters from an Automobile Industry by Iron Oxide-Coated Sand'**, by **SAMIR BAJPAI**, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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ABSTRACT

Feasibility of treatment of copper-plating and zinc-plating wastewaters from an automobile industry (Lohia Machines Limited (LML), Kanpur) by iron oxide-coated sand (IOCS) was investigated. Based on preliminary tests and practical considerations, one-step IOCS treatment appeared nonfeasible The study showed suitability of IOCS treatment as a polishing unit for the existing wastewater treatment (alkaline chlorination, neutralisation and settling) to improve the effluent quality. Coating with ferric nitrate and sodium hydroxide together produced the best IOCS in terms of iron oxide content, longevity and durability, and metal removal. Detailed column tests (column ID 2 54 cm, IOCS depth 45 cm, hydraulic loading rate 0.108 m^3/m^3 min (EBCT 9.3 min) and 0.0647 m^3/m^3.min (EBCT 15.5 min), copper 3 1-3.86 mg Cu/L and zinc 3 26-5.76 mg Zn/L) showed excellent removal of copper and zinc up to 110 and 150, and 35 and 70 bed volumes for empty bed contact time of 9.3 and 15 5 min, respectively from the aerated neutralisation tank effluent. Five cycles of detailed column tests, using a hydraulic loading rate of 0.108 m^3/m^3.min (EBCT 9.3 min) including regeneration by 0 03 M $NaNO_3$ at pH 2.0 after a throughput of 150 bed volume, further indicated suitability of IOCS in the removal (effluent copper and zinc below 0.1 mg Cu/L and 3.0 mg Zn/L throughout) and recovery (copper 81.26%-92.89% and zinc 76.13%-88.53%) of copper and zinc. However, optimisation of the process in terms of aeration requirements, hydraulic loading rate, and IOCS depth for copper and zinc removal as well as the regeneration procedure (regenerant, pH and duration) for copper and zinc recovery needs to be addressed in more detail.

1. INTRODUCTION

Any metal article before being put to the desired use has to undergo a series of processes, known as metal finishing, such as cleaning and pickling, smoothening or roughening, depositing another metal on it by chemical exchange or by electroplating, coating it with organic material, or oxidising it by electrolysis so as to improve the surface of the basic material by providing such improvements as corrosion resistance, durability, aesthetic appearance and electrical conductivity according to the process(es) used Electroplating is a process of electrodeposition by which a thin, smooth, sound metallic coating is produced over a basic material. This coating provides corrosion protection, wear or erosion resistance, anti-frictional characteristics, lubricity, electrical conductivity, heat and light reflectivity, or other special surface characteristics enabling the basis material to be used for various purposes. Automobile industry, in general, employs metal plating (copper and zinc) and finishing as a significant part of its total activity.

The wastes generated by electroplating and metal finishing operations contain heavy metals. Heavy metals and their salts are potentially hazardous to terrestrial and aquatic life, and to human health. They include all metals with atomic number greater than 23 and specific gravity more than 5 (The Condensed Chemical Dictionary, 1977). Much has been reported on the adverse effects of heavy metals on plant, animal and man because these metals are non-degradable, persist in nature for a longer period, are toxic to living organisms at fairly low concentrations and tend to either biologically magnify or accumulate in plant or animal systems (Förstner and Wittmann, 1981; Connell and Miller, 1984). Regardless of the source, heavy metal-bearing metal-finishing and metal-plating wastes eventually end up in surface and subsurface waters (Hasan et al., 1986). As the global awareness towards the potential toxicity of heavy metals is increasing, the effluent standards are becoming more stringent. Hence, it is mandatory for any industry to remove/recover such metals through suitable treatment before disposal.

Conventional methods of removal/recovery of metals from metal-finishing and metal-plating wastewaters include neutralisation/precipitation, adsorption and ion exchange. All these methods have their inherent benefits and limitations. Recently, a novel method, adsorptive filtration by iron oxide-coated sand, has been proposed by Edwards and Benjamin (1989b) in an attempt to circumvent the limitations of the conventional methods. In laboratory tests, the method has been found useful in removing metals such as copper, chromium, cadmium, lead and nickel from synthetic waste solutions (Edwards and Benjamin 1989b; Benjamin and Sletten 1992; Lai et al., 1994 and Benjamin et al., 1996) and zinc (Benjamin and Sletten, 1992), copper (Benjamin et al., 1996) and cadmium (Satpathy and Chaudhuri, 1995) from metal-bearing wastewaters. The present study was undertaken to assess suitability of iron oxides-coated sand for treatment of metal-plating wastewaters from an automobile industry —— copper-plating and zinc-plating wastewaters from the Lohia Machines Limited (LML), Kanpur.

2. BACKGROUND INFORMATION AND SCOPE

This chapter is aimed at providing a background for the study and its scope A brief discussion on metal plating and metal-plating wastewater treatment including characteristics of the metal-plating wastewaters at the Lohia Machines Limited (LML), Kanpur is presented. Available information on removal of heavy metals by iron oxide-coated sand is also included. Finally, the scope of the study is outlined

2.1 Metal Plating and Metal-Plating Wastewater Treatment at the Lohia Machines Limited (LML), Kanpur

At LML, copper-plating and zinc-plating are being employed for different automobile parts For copper plating, alkaline cyanide bath and acid sulfate bath are being used while for zinc plating, alkaline cyanide bath is in use, and the plating is carried out in batch in still tanks where articles are processed on racks. Articles to be plated in alkaline cyanide baths are given a pretreatment involving hot-soak alkaline degreasing at 80°-90°C followed by anodic alkaline clean at 80°-90°C to remove oil, grease and dirt from the surface of the base material; after a water rinse they are given acidic etching using 30% H_2SO_4 solution to remove the oxide films from the surface and to get a mat or nonspecular surface. This is followed by a water rinse and then the article is dipped in 5% sodium cyanide alkaline bath followed by a water rinse again. Now the article becomes ready for plating.

For copper plating, usual compositions of the cyanide-copper plating bath are: copper cyanide 70-80 g/L, sodium cyanide 90-100 g/L, sodium hydroxide 30-40 g/L and free sodium cyanide 10-12 g/L.

The bath is operated at 70°C and pH > 10 0, and with cathode and anode current densities of 0 06-0.07 and 0 025-0 03 amp/sq cm, respectively For zinc plating, the compositions of the cyanide-zinc plating bath are. zinc cyanide 75-80 g/L, sodium cyanide 55-65 g/L, sodium hydroxide 80-90 g/L and sodium polysulfide 1.5 g/L with some proprietary brightener. The bath is operated at 35-40°C and with current density of 0.045 amp/sq cm. After plating, the articles are sent for rinsing and then drying.

Articles on which a thick, even copper coating is desired are plated in acid sulfate bath First, the articles are given acid pickling in 10% H_2SO_4 solution followed by a water rinse and then they are put in copper sulfate bath having 150-160 g/L copper sulfate and 60-70 g/L H_2SO_4 at 40°C After plating the articles are rinsed and dried.

The metal-plating wastewaters at the LML can be divided into two categories, viz concentrated solution resulting from discharge of the spent plating baths and dilute rinse water from cleaning/rinsing operations (Fig.1). Plating baths are discharged intermittently, whereas rinse water is discharged on a continuous flow basis Waste streams from different operations are first taken to an oil and grease trap to remove water immiscible oil, grease and solvents, and from there the waste streams are taken to an equalisation tank so as to control the rate of flow of the wastewaters to be treated and to dilute the concentrated plating bath solutions. From the equalisation tank, the mixed wastewater is taken for oxidation of cyanide to CO_2 and N_2 by alkali-chlorination. Alkaline chlorination of wastewater is done in batches — 10% sodium hydroxide and 10% sodium hypochlorite solutions are added to the tank and an oxidation period of 30-40

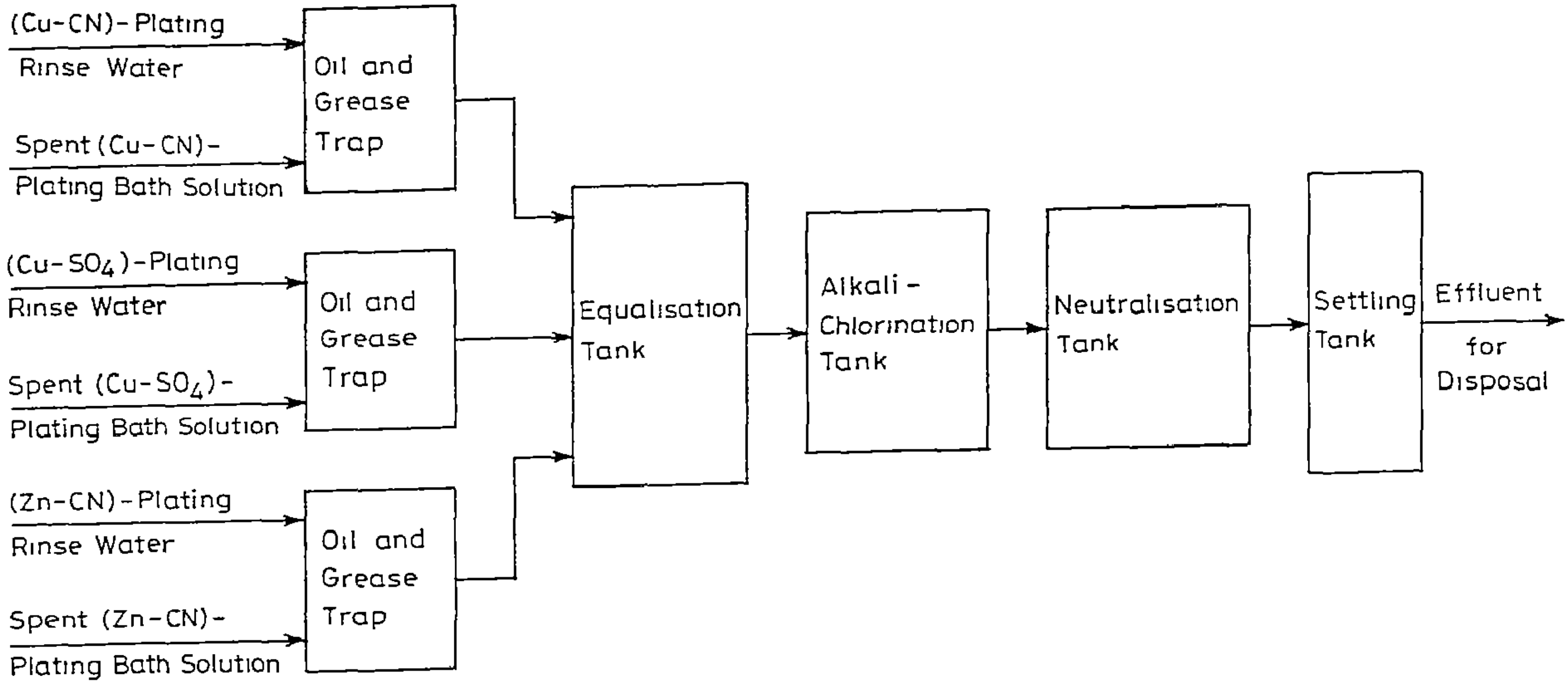

Fig. 1 Treatment schematic of the metal-plating wastewater at the LML, Kanpur.

minutes is provided with pH maintained above 10.0 The hypochlorite added oxidizes the cyanide to cyanogen chloride which is a volatile, toxic and odorous gas but in presence of caustic, sodium cyanate is formed from the cyanogen chloride which is only about one-thousandth as toxic as cyanide (Eckenfelder, 1989)

$$NaCN + Cl_2 \longrightarrow CNCl + NaCl$$

$$CNCl + 2NaOH \longrightarrow NaCNO + H_2O + NaCl$$

After alkaline chlorination, the wastewater is taken to a neutralisation tank where its pH is brought down to 7-8 by treatment with 10% H_2SO_4 solution. At this pH, in presence of excess chlorine, the cyanate is converted to CO_2 and N_2.

$$2NaCNO + 4NaOH + 3Cl_2 \longrightarrow 2CO_2 + 6NaCl + N_2 + 2H_2O$$

The treated wastewater is taken to a settling tank where metal hydroxides formed are settled and the effluent is discharged to the sewer. The settled sludge is dried in sludge drying beds and the dried sludge cakes are disposed of as landfill.

2.2 Characteristics of Copper-Plating and Zinc-Plating Wastewaters at the LML, Kanpur

Samples of the copper-plating and zinc-plating wastewaters at the LML, Kanpur were collected from three locations — from the outlet end of the equalisation tank, from the outlet end of the neutralisation tank and from the outlet end of the settling tank. Samples were analysed for pH, temperature, conductivity, acidity and alkalinity, suspended and dissolved solids, copper, zinc, cyanide and sulfate. An atomic absorption spectrometer (Spectr AA-20, Varian) was used for determination of copper and the Zincon method (Standard Methods, 1992) was used for determination of zinc. A titrimetric method was used for determination of cyanide and sulfate was measured using a turbidimetric method (Standard

Methods, 1992) Methods outlined in the Standard Methods (1992) were employed for all other parameters Characteristics of the wastewaters are shown in Table 1

As the pH neutralisation takes place immediately after the alkaline chlorination and the contents of both tanks are continuously stirred, the expected benefit of formation of metal hydroxides in alkaline chlorination tank is lost Though some metal hydroxide precipitation takes place in the settling tank (pH 7-8.5), it is not enough to render the effluent metal concentrations to within the permissible limits most of the times. Also, according to Patterson (1985) and Yost and Scarfi (1979a, 1979b), for copper and zinc cyanide plating solutions, higher optimum treatment pH of 12.0-13 0 for copper and 10.0 for zinc precipitation are required because of major interfering effects on copper and Zinc solubility due to the presence of high concentrations of carbonate ions formed as a result of decomposition of cyanide Treatability studies by Yeats (1977) also confirm this carbonate influence. Due to the above reasons, most of the times the effluent from the LML, Kanpur contains metal concentrations significantly higher than the permissible limits (copper 3.0 mg Cu/L and zinc 5 0 mg Zn/L for discharge into inland surface waters (IS :2490-1974)) Also, as the emphasis now a days is on total metal removal and recovery of precious metals like copper, the wastewater treatment at the LML needs some modifications so as to meet the future stringent effluent standards and economically beneficial recovery of precious metals like copper.

Table 1 : Characteristics of metal-plating wastewaters at the LML, Kanpur.

	Equalisation Tank Effluent	Neutralisation Tank Effluent	Settling Tank Effluent
pH	6.8-8.6	6.4-8.2	7.1-8.5
Temperature (°C)	30.8-32.4	31.4-32.6	30.5-31.8
Conductivity (μmho/cm)	3028-3251	3125-3220	2089-2721
Alkalinity (mg $CaCO_3$/L)	546-768	680-760	698-736
Acidity (mg $CaCO_3$/L)	38-220	65-208	42-98
Suspended solids (mg/L)	88-138	142-187	22-46
Dissolved solids (mg/L)	998-1204	978-1440	1201-1490
Sulfate (mg SO_4^{2-}/L)	16-21	20-32	8-22
Cyanide (mg CN /L)	3.21-11.2	0.15-1.1	0.12-0.85
Copper (mg Cu/L)	4.3-10.7	3.1-7.4	2.9-6.3
Zinc (mg Zn/L)	3.7-11.3	2.7-8.2	1.7-7.6

2.3 Removal of Heavy Metals by Iron Oxide-Coated Sand (IOCS)

It has long been recognised that if the adsorbent (solid surface) is chosen carefully and the solution chemistry is adjusted appropriately, adsorption- based processes are capable of removing metals over a wide pH range and to much lower levels than processes based on precipitation (Dugger et al., 1964, James and Healy, 1972, Shindler et al , 1976, Benjamin, 1983). In addition to offering more reliable and more efficient removal of uncomplexed cationic metals, adsorption processes can often remove inorganically- and organically-complexed metals that would not be removed by a conventional treatment methodology (Davis and Leckie, 1978; Elliot and Huang, 1980, Benjamin and Leckie, 1982, Bowers and Huang, 1986). Removal of Heavy metals using adsorptive filtration by iron oxide-coated sand, proposed by Edwards and Benjamin (1989b), combines the advantages of the process of adsorption and filtration for effective removal of soluble (cationic, anionic or complexed) and particulate metals.

Amorphous iron oxide (ferrihydrite) is an excellent regenerable adsorbent. In a laboratory study (Edwards and Benjamin, 1989a), ferrihydrite (formed by reacting ferric nitrate and sodium hydroxide) was shown to remove copper, cadmium, zinc, nickel and trivalent chromium from both synthetic and real metal-plating wastes to levels lower than that attainable by precipitation. Ferrihydrite is formed in conventional metal-plating waste treatment by precipitation of iron salts which are often added to help coagulate precipitated metal oxides or hydroxides. Metal removal by adsorption onto ferrihydrite is an important side benefit of this practice. Since adsorption processes are most effective when large quantities of adsorbent are present, increasing the coagulant dose leads to improved treatment efficiency in most cases But the iron oxides sludge formed is difficult to de-water (it is a bulky, hydrated, amorphous, flocculant material with extremely low hydraulic conductivity) and, therefore, add substantially to the volume of sludge and costs of disposal Thus, optimisation of the metal removal efficiency requires that large amount of iron oxides be available, but optimisation of the sludge processing step requires that minimal amount of this material be disposed of. With these considerations, Edwards and Benjamin (1989b) developed methods of coating sand with iron oxide to produce an adsorbent with greater flexibility in application, combining the advantages of adsorption and filtration processes. As this idea came in vogue, researchers have come up with different coating techniques and have reported success in removal/recovery of free cationic, anionic, dissolved and particulate, and complexed metals from synthetic as well as real metal-plating solutions.

Edwards and Benjamin (1989b) applied coating by evaporating (110 ± 10°C for 20 h) 20 g of $Fe(NO_3)_3.9H_2O$ in presence of 200 g of dried sand and enough water (about 50 mL) to cover the sand. Using this process, approximately 75% of the added iron remained attached to the sand after washing. The final iron surface concentrations were 10 mg Fe/g of sand. The coating was found to be durable in agitated conditions and was resistant to acid solutions. The iron oxide-coated sand outperformed uncoated sand in removing both uncomplexed (Cu, Ni, Cr(III), Cd, Pb) and ammonia-complexed (Cu, Zn, Cd) soluble metals. They also reported that the coated sand could filter particulate metals out of suspension more efficiently than could conventional (uncoated) filter sand

Satpathy and Chaudhuri (1995), using the same coating technique, have reported good, one step removal/recovery of cadmium from cadmium and cyanide electroplating wastewaters IOCS columns were regenerated by a 10^{-2} M $NaNO_3$ solution adjusted to pH 3 0 with nitric acid and following regeneration, the column was equilibriated using a 10^{-2} M $NaNO_3$ solution adjusted to pH of the wastewater. Using the same coating technique, Benjamin and Sletten (1992) reported good removal (effluent levels less than 0.2 mg/L of total zinc and less than 0 1 mg/L of soluble zinc) of zinc from a treated (precipitation and settling at pH 8 0), zinc-bearing wastewater

Bailey et al (1992), using a modified coating technique (sodium hydroxide was mixed with 80 mL of 2.0 M ferric nitrate solution or 80 mL of 2.47 M ferric chloride solution and poured over 200 mL of bulk sand, mixed well and dried at 110°C for 14 hours), reported more than 99% removal of hexavalent chromium from a 20 mg/L Cr(VI) synthetic waste solution. Lai et al. (1994) reported complete removal of copper from a synthetic copper solution (0.64-3.2 mg/L) up to 35-45 bed volumes by IOCS prepared by heating sand in presence of a precipitate formed by addition of sodium hydroxide to ferric nitrate solution

Recently, Benjamin et al. (1996) have reported a further modified coating technique in which IOCS were coated in two steps. In the first step, 80 mL of 2.5 M $FeCl_3$ solution was poured over 200mL bulk sand and the mixture was heated at 110°C for 3 h and then again at 550°C for 3 h, cooled and then 40 mL of this coated sand were mixed with 80 mL of 2 1 M $Fe(NO_3)_3$ and 0 6 mL of 10 M NaOH or 80 mL of 2.5 M $FeCl_3$, and heated at 110°C for 10-14 h, cooled and then again heated for 3 h at 110°C For coating with $FeCl_3$, seven such cycles of heating for 3 h at 110°C and cooling were repeated. Using the above media, successful removal of uncomplexed and ammonia-complexed cationic metals (Cu, Cd, Pb, Ni, Zn) as well as some oxyanionic metals (SeO_3, AsO_3) from simulated and actual waste streams over a wide range of metal concentrations have been reported The adsorbent was stable during backwashing and regeneration operations, releasing most metals quantitatively except AsO_3.

2.4 Scope

Adsorptive filtration using IOCS appeared to be a novel and effective method capable of circumventing the disadvantages of the conventional methods of metal-plating waste treatment. However, the work reported so far concentrated primarily on the removal of metals from synthetic waste solutions or simulated plating-waste solutions. More recently, Satpathy and Chaudhuri (1995) reported successful use of IOCS in one-step treatment of cadmium-plating wastewater. It was thought appropriate to undertake a laboratory study to assess the suitability of IOCS for treatment of common metal-plating wastewaters of the automobile industry, viz. copper-plating and zinc-plating wastewaters. The study was undertaken using the copper-plating and zinc-plating wastewaters from a scooter manufacturing industry, the Lohia Machines Limited (LML), Kanpur and conducted along the following lines.

a. Investigate the suitability/usefulness of iron oxide coating methods in terms of iron oxide retention, longevity and durability, and metal removal, and come up with an appropriate coating method b Conduct preliminary tests to assess the feasibility of using IOCS for removing copper, zinc and cyanide from the copper-plating and zinc-plating wastewaters, and to decide on the feasibility of the process either as one-step treatment or as a polishing unit for the existing wastewater treatment to improve the effluent quality

c Conduct detailed tests on the process.

3. IRON OXIDE-COATED SAND

Iron Oxide-Coated Sand (IOCS) was prepared by three different methods and were characterised in terms of their iron content, longevity and durability, and suitability/usefulness in metal removal.

3.1 Preparation of IOCS

Locally available river sand (sieved to a geometric mean size of 0.71 mm, acid washed (pH 1.0, 24 h), rinsed in triple-distilled water and dried at 105°C) was coated with iron oxide employing three different methods of coating. In the first method as suggested by Edwards and Benjamin (1989b), 200 g of dried sand, 20 g of $Fe(NO_3)_3.9H_2O$ and enough water (about 50 mL) to cover the sand were placed in a conical flask and following 2 min of gentle agitation, the uncovered flask was placed in a drying oven (110 ± 10°C) for 20 h. The coated sand was washed with triple-distilled water until the run-off was clear, dried overnight at 110 ± 10°C and stored in capped bottles. The coated sand was designated as IOCS-1.

In the second method, 200 g of dried sand were mixed with 80 mL of 2.0 M $Fe(NO_3)_3$ solution and dried at 110 ± 10°C for 20 h in a drying oven. The coated sand was washed with triple-distilled water until the run-off was clear, dried overnight at 110 ± 10°C and stored in capped bottles. The coated sand was designated as IOCS-2.

In the third method as suggested by Bailey et al. (1992), 300 g of dried sand was mixed with 80 mL of 2 0 M $Fe(NO_3)_3$ solution in a conical flask, and 15 M sodium hydroxide solution was added drop wise and mixed till the pH of the mixture was 10-11. The uncovered flask was then placed in a drying oven (110 ± 10°C) for 20 h and the contents of the flask were stirred and mixed with a spoon every 4 h. After drying, the coated sand was washed with triple-distilled water until the runoff was clear, dried overnight at 110 ± 10°C and stored in capped bottles. The coated sand was designated as IOCS-3.

3.2 Iron Content, Longevity and Durability of IOCS

To compare the iron content of the IOCS prepared by the three methods, an analysis of the wash water for iron was done, and also, 5.0 g of coated sand were digested in warm 10% HNO_3 for 2 h and the amount of iron dissolved was measured using an atomic absorption spectrometer (Spectr AA-20, Varian). It was found that IOCS-3 had the maximum iron content (7.4 mg Fe/g sand; 2.5% Fe by weight) followed by IOCS-2 (4.3 mg Fe/g sand, 2.1% Fe by weight) and IOCS-1 (3.6 mg Fe/g sand, 1.8% Fe by weight).

To compare their longevity and the strength of the iron oxide coating, the three IOCS were subjected to agitation in an end-over-end shaker under acid condition. IOCS (10 g)was placed in 100 ml of triple-distilled water adjusted to pH 2.0, put in an end-over-end shaker at 20 rpm and the iron solubilised was measured as a function of time (Fig. 2). It was found that total per cent solubilisation after 150 min of agitation was the least for IOCS-2, but for an initial period of 40 min IOCS-3 showed the least solubilisation of the iron oxide coating (below 2%).

3.3 Suitability/Usefulness of IOCS in Metal Removal

Downflow column tests were employed to assess the suitability/usefulness of the three IOCS in metal removal. Column tests were conducted in 1.1 cm ID glass columns with 18 cm medium depth and at a flow rate of 3.0 mL/min (empty bed contact time

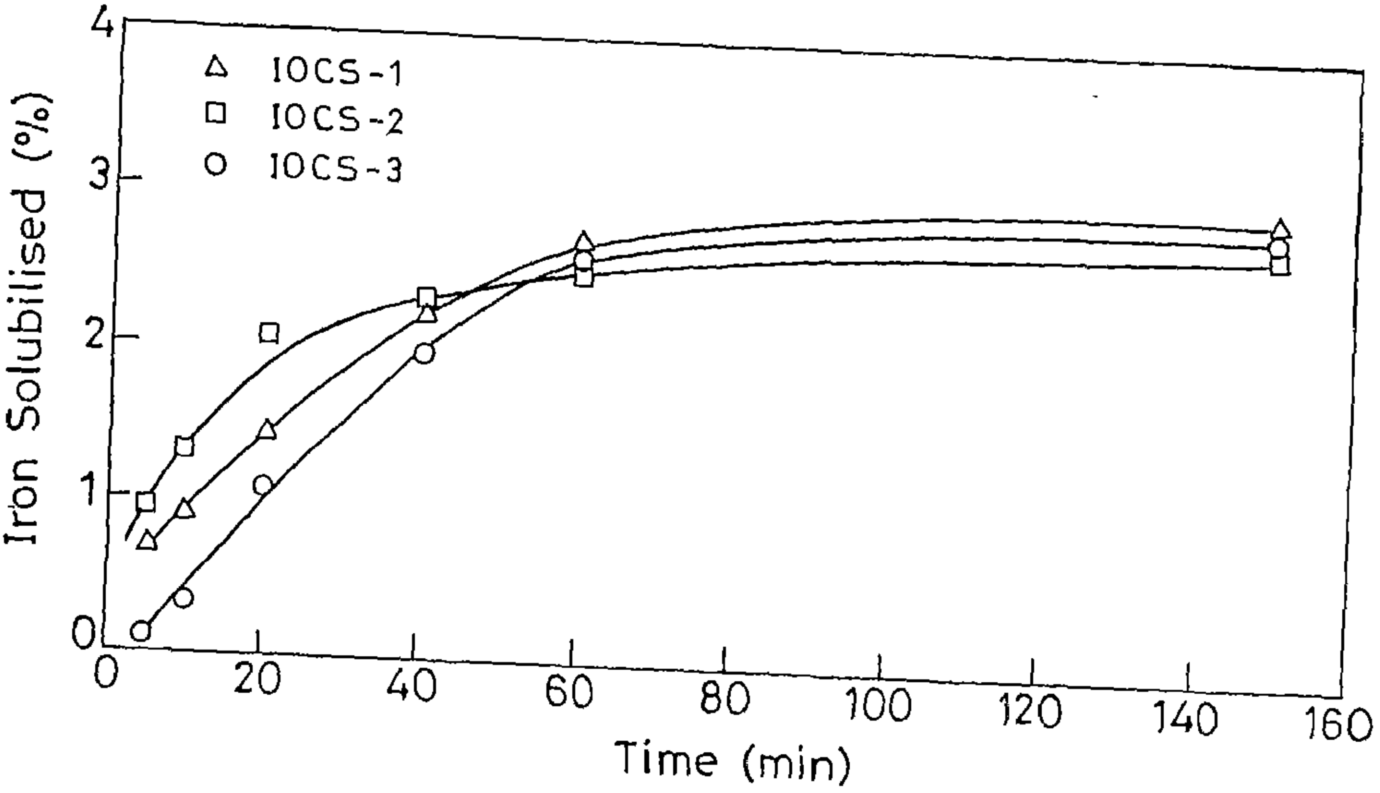

Fig. 2 Solubilisation of iron oxide coating.

5 70 min) using a synthetic copper solution (copper 3 2 mg Cu/L, Ionic strength (I) 0 1 M, pH 7.0). The columns were run for 24 h IOCS-3 outperformed IOCS-1 and IOCS-2 in removing copper (Fig.3)

Based on the findings that IOCS-3 had the maximum iron content, exhibited higher to comparable longevity/durability among the IOCS prepared by three different methods and showed the best performance in metal removal, it was decided to use IOCS-3 in tests on the metal-plating wastewater treatment.

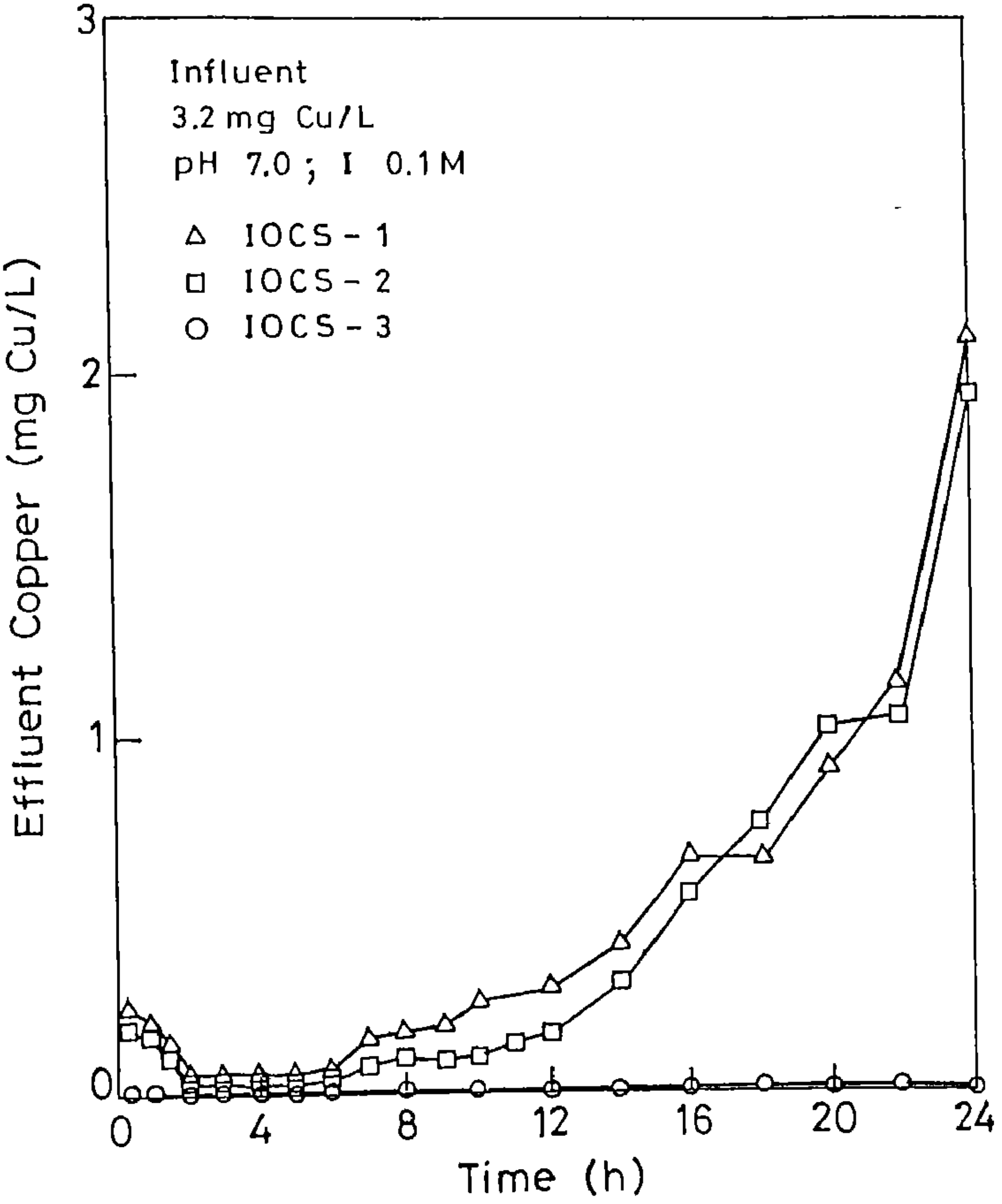

Fig. 3 Removal of copper by IOCS in column test.

4. FEASIBILITY OF ONE-STEP IOCS TREATMENT FOR METAL-PLATING WASTEWATERS AT THE LML, KANPUR

The effluent characteristics (copper 2.9-6.3 mg Cu/L, zinc 1.7-7.6 mg Zn/L and cyanide 0.1-0.85 mg CN^-/L) of the metal-plating wastewaters at the LML, Kanpur clearly indicate the inefficiency of the existing wastewater treatment. This necessitated an investigation to assess the feasibility of using IOCS for removing copper, zinc and cyanide from the copper-plating and the zinc-plating wastewaters with a view to decide on the applicability of the process either as one-step treatment or as a polishing unit for the existing wastewater treatment to improve the effluent quality.

Of the various cyano complexes of metals, zinc and cadmium complexes are reported to be very unstable, and their almost complete dissociation occurs in dilute solutions at any pH (Doudoroff, 1956; Benefield et al., 1982; Standard Methods, 1992). On the other hand, in equally dilute solutions, much less dissociation of the more stable cyanide complexes formed with copper(I) occurs (Standard Methods, 1992). As discussed in chapter 2, successful removal of zinc from synthetic as well as actual metal-bearing wastewaters by IOCS were reported (Edwards and Benjamin 1989b; Benjamin and Sletten, 1992, Benjamin et al., 1996). Also Satpathy and Chaudhuri (1995) reported successful one-step treatment for removal of cadmium and cyanide from plating wastewater having cyano complexes quite similar to the cyano complexes of zinc in behaviour (Sharpe, 1976). On the other hand, treatment of synthetic or actual copper-plating wastewater containing copper and cyanide by IOCS has not been reported.

Patterson (1985) emphasised the need for destruction of copper-cyanide complex for efficient treatment of copper-plating wastewater Further, use of iron salts for treatment of strong transition metal (M^{2+}) complexes by precipitation as ferri-ferro or ferro-ferro cyanide (Watson, 1973) or as $M_2[Fe(CN)_6]$ (Bonan et al., 1994) has been reported. Hence, it was considered appropriate to conduct preliminary tests to assess the feasibility of using IOCS for removing copper and cyanide from copper-plating wastewater with the premise that iron present in IOCS would cause the copper-cyanide complex to be removed as $Cu_2[Fe(CN)_6]$. Batch and column tests were conducted using diluted (10^4 times) copper-plating bath solution.

4.1 Batch and Column Tests

To get an idea about the empty bed contact time (EBCT) to be used in column tests, a batch sorption kinetic test was performed using a synthetic copper solution (copper (total) 6.2 mg Cu/L; copper (filtered) 5.7 mg Cu/L; ionic strength 0.03 M; pH 6). To 100 mL of the synthetic copper solution 5.0 g of IOCS were added and placed in an end-over-end shaker (20 rpm) Samples were withdrawn at selected time intervals and analysed for total and filtered (0.45 µm) copper Good removal of copper was observed, and bulk of the sorption occurred in the initial 15 min (Fig 4)

Batch sorption test (5.0 g IOCS; 100 mL of 10^4 times diluted plating-bath solution — copper 5.9 mg Cu/L, CN^-(free) 11.2 mg CN^-/L; pH 8 8) and column test (Column ID 1.1 cm, IOCS medium depth 20 cm, EBCT 13 min) both showed little removal of copper and cyanide from the diluted copper plating-bath solution (data not shown). It appeared necessary to conduct more tests to investigate the behaviour of Cu-CN complex *vis-a-vis* IOCS treatment.

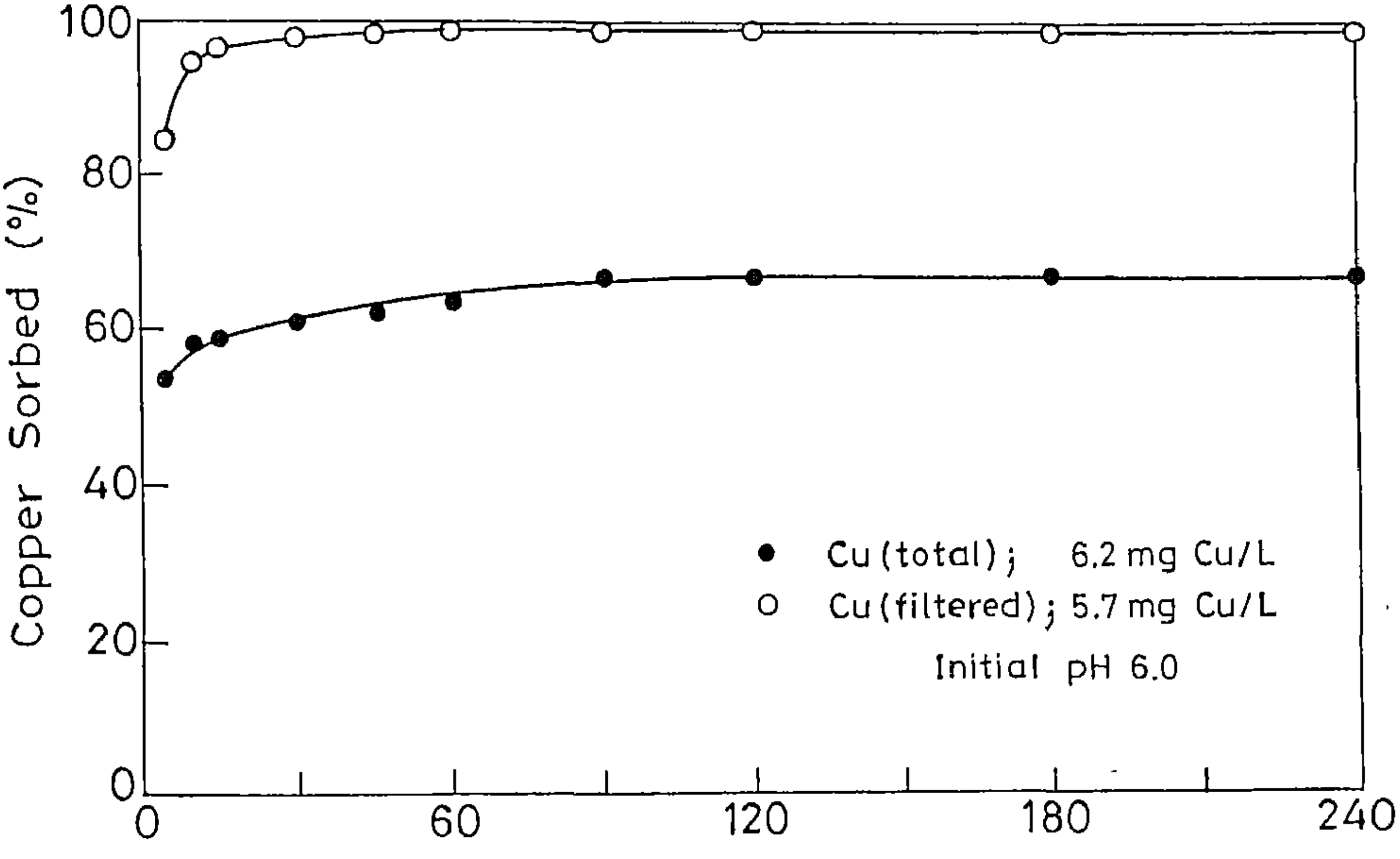

Fig. 4 Batch copper sorption kinetic test.

Possible cyano complexes of copper are $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{3-}$ among which $[Cu(CN)_4]^{3-}$ is the most stable (Sharpe, 1976). In the copper -plating wastewater, all copper and cyanide existed in the form $[Cu(CN)_4]^{3-}$. As the pH of zero point of charge (pHzpc) of IOCS is 9.0-9.3 (Satpathy and Chaudhuri, 1995; Benjamin et al., 1996) and use of iron salts for treatment of strong transition metal (M^{2+}) complexes by precipitation with iron as ferri-ferro cyanide (Watson, 1973) or as $M_2[Fe(CN)_6]$ (Bonan, 1994) has been reported, it was thought appropriate to lower the pH of the wastewater in presence of an iron salt so as to minimise escape of free CN^- as HCN and take advantage of the more positive IOCS surface in sorptive removal. For this, $Fe(NO_3)_3$ solution served the purpose because of its acidic nature. To 1 L of the diluted (10^4 times) copper-plating bath solution 1 mL of 2M $Fe(NO_3)_3$ solution was added and the pH went down from 8.8 to 6.7. In a column test (column ID 1.1 cm; plain sand or IOCS media depth 20 cm; EBCT 13 min; copper 6.35 mg Cu/L) not much removal of copper (30-36%) was observed, though substantial reduction in free CN^- occurred— from 11.2 mg CN^-/L to 5.5 mg CN^-/L following addition of $Fe(NO_3)_3$ and from 5.5 mg CN^-/L to almost nil in the column (Fig. 5).

In a further column test, following addition of $Fe(NO_3)_3$ to the diluted (10^4 times) copper plating - bath solution, the pH was further lowered (from 6.7 to 4.5) using 10% HNO_3. Good removal of both copper (Fig. 5) and cyanide was observed.

4.2 Directions for Further Tests

It is apparent that for effective one-step treatment of a metal-plating wastewater containing cyano complexes, destruction of the stable cyano complexes would be necessary. It is also

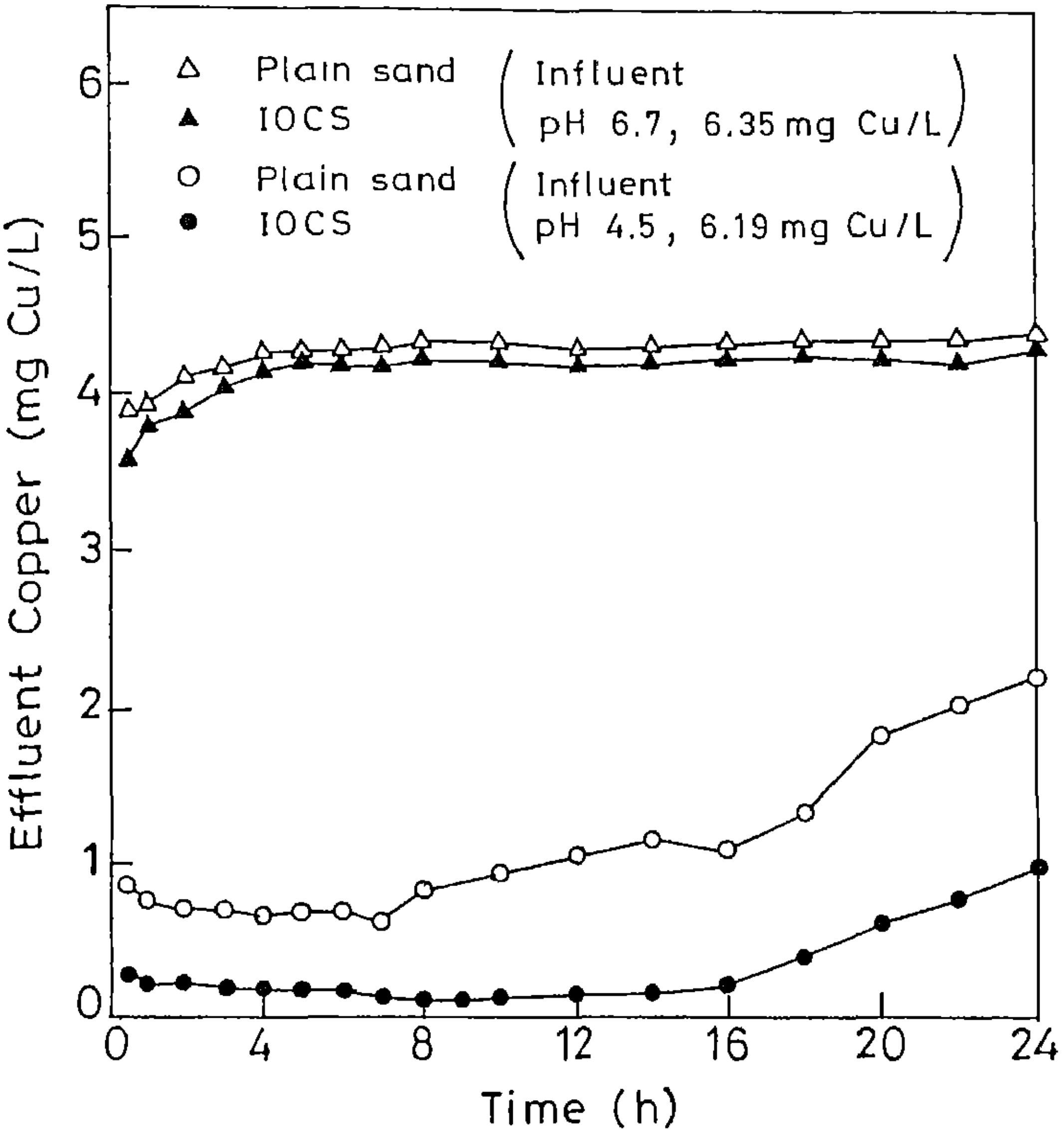

Fig. 5 Removal of copper in column test from diluted copper-plating bath solution following ferric nitrate addition.

supported by the literature evidence (Patterson, 1985) Based on the results of the preliminary tests, the approach would be to collect the equalisation tank effluent in a closed container, bring down its pH to 3-4, pass compressed air to force out the HCN evolved to be absorbed by NaOH (cyanide recovery), and pass the wastewater now free of cyanide through an IOCS column for copper removal. Though attractive in terms of one-step treatment for copper and cyanide recovery, this approach would require elaborate set-up and highly skilled operation. Possibility of accidental release of HCN could not be ruled out. Based on these considerations, this approach did not appear feasible. Keeping the existing wastewater treatment at the LML, Kanpur in perspective, the second approach would be to settle the effluent of the neutralisation tank following alkaline chlorination and pass it through an IOCS column as a polishing unit. This approach was selected for further detailed tests.

5. IOCS TREATMENT AS A POLISHING UNIT

Based on practical considerations and keeping the existing wastewater treatment at the LML, Kanpur in perspective, IOCS treatment as a polishing unit was selected for further detailed tests.

5.1 Batch Sorption and Preliminary Column Tests

As discussed in chapter 2, apart from cyanide the other major interfering ion in the treatment of metal-plating wastewater is carbonate, and for effective treatment, this excess carbonate would require prior removal. One possible approach, as suggested by Patterson (1985), would be air stripping at near neutral pH. Batch sorption tests (4 h) were conducted using settled (3 h) and aerated (4 h) effluent from the neutralisation tank (pH 7.8 - 8.0; copper (total) 3.07-3.2 mg Cu/L; copper (filtered) 0.27-0.29 mg Cu/L; zinc (total) 4.08 - 4.85 mg Zn/L and zinc (filtered) 3.36 - 3.48 mg Zn/L) and settled (3 h) nonaerated effluent (pH 6.8 - 7.2; copper (total) 3.44-3.5 mg Cu/L; copper (filtered) 0.37-1.37 mg Cu/L; zinc (total) 4.21-5.23 mg Zn/L and Zinc (filtered) 3.44 - 4.84 mg Zn/L) using both IOCS and plain sand (50 g/L). Preliminary column tests (24 h) (column ID 1.1 cm; medium depth 20 cm; EBCT 13 min) were also conducted using settled (3 h) and aerated (4 h) effluent (pH 7.2; copper 6.2 mg Cu/L and zinc 3.8 mg Zn/L) and settled (3 h) nonaerated effluent (pH 6.8; copper 5.9 mg Cu/L and zinc 3.7 mg Zn/L) using both IOCS and plain sand. The results of both batch tests (Fig. 6 and 7) and column tests (Table 2) clearly established the superiority of IOCS in the removal of coper and zinc from the aerated neutralisation tank effluent.

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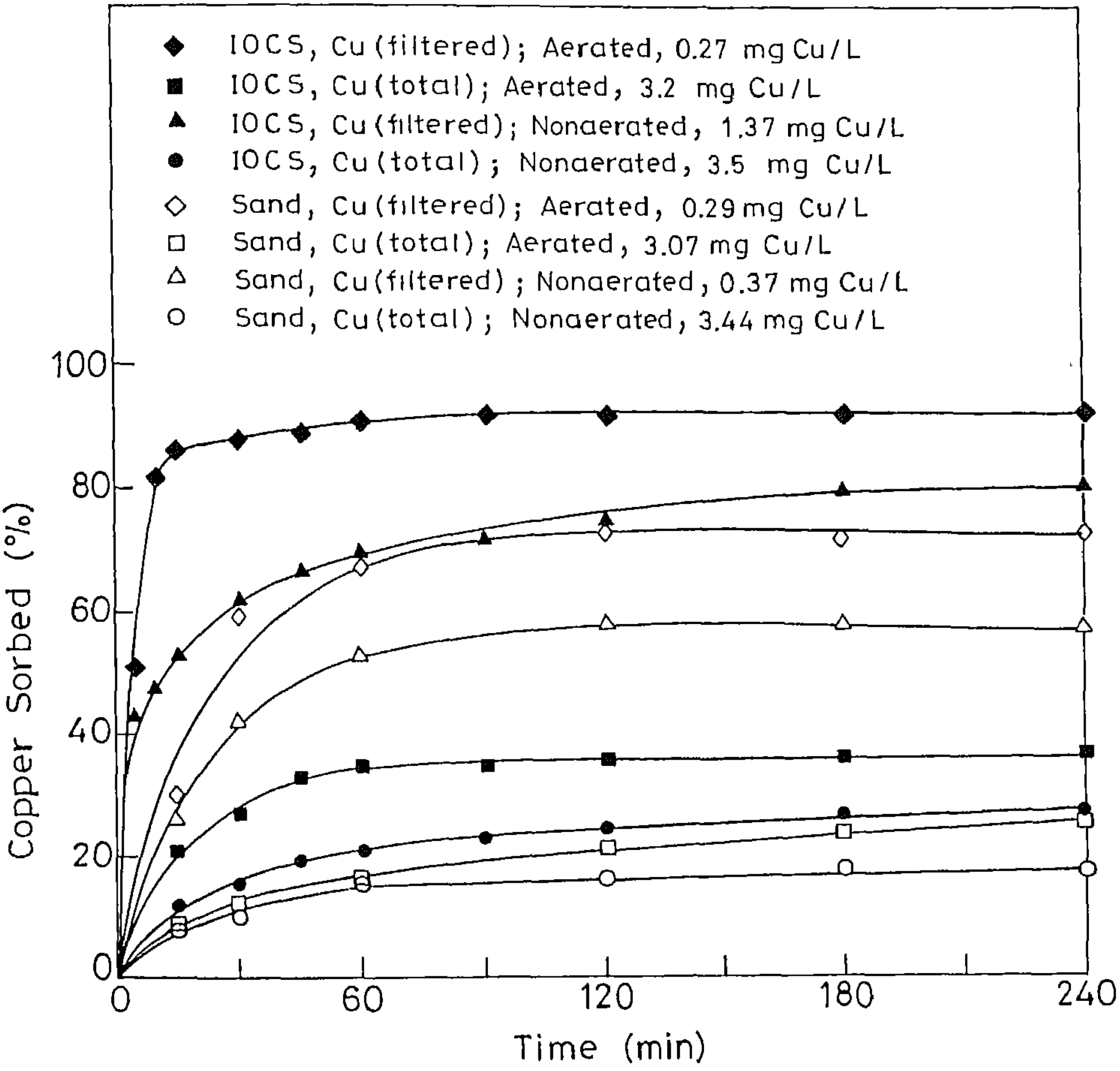

Fig. 6 Effect of aeration on sorption of copper from neutralisation tank effluent by sand and IOCS in batch sorption tests.

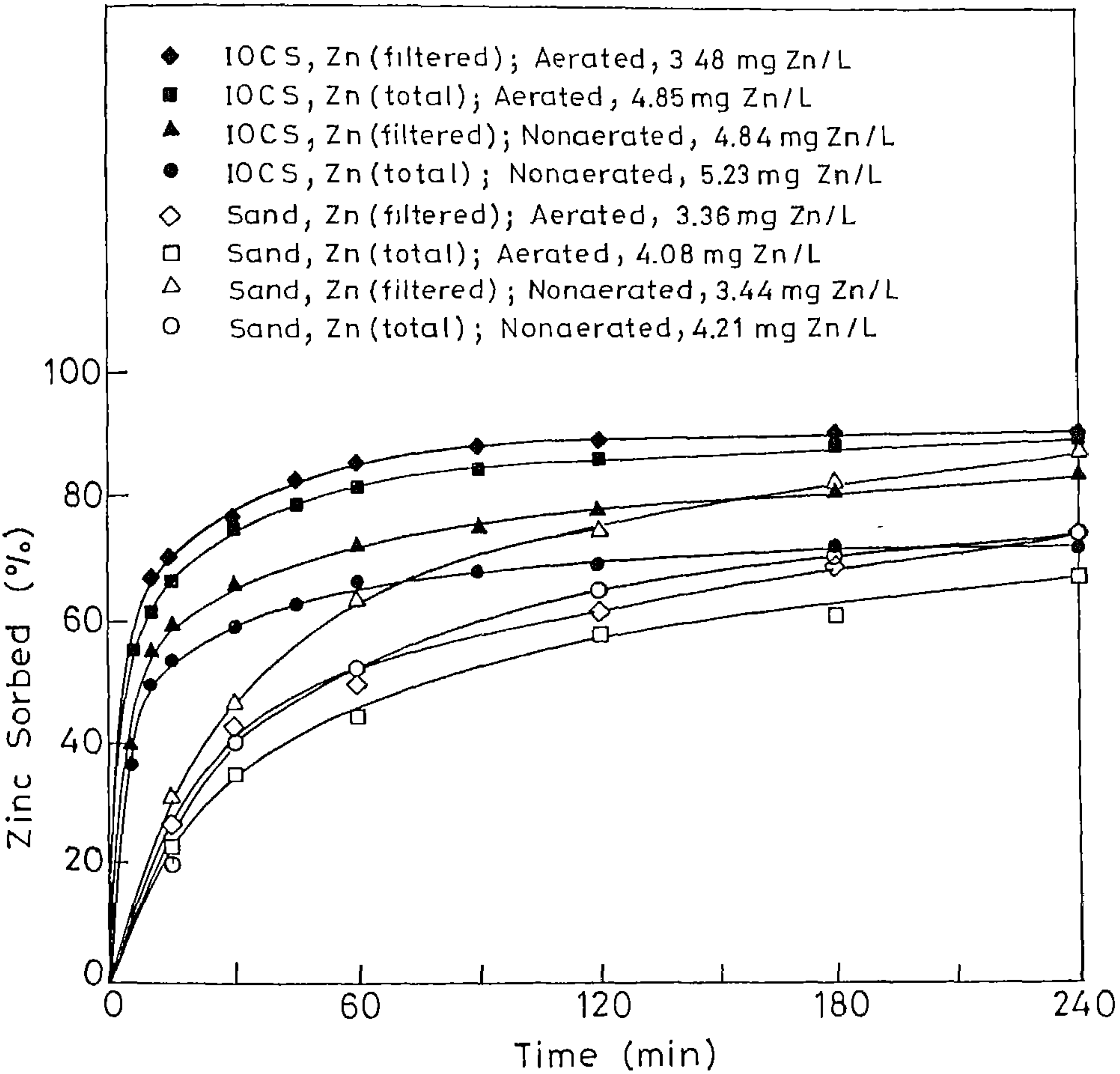

Fig. 7 Effect of aeration on sorption of zinc from neutralisation tank effluent by sand and IOCS in batch sorption tests.

Table 2 : Effect of aeration on removal of copper and zinc by sand and IOCS in preliminary column tests.

Time (min)	Effluent Copper (mg Cu/L)				Effluent Zinc (mg Zn/L)			
	Plain Sand (Nonaerated)	IOCS (Nonaerated)	Plain Sand (Aerated)	IOCS (Aerated)	Plain Sand (Nonaerated)	IOCS (Nonaerated)	Plain Sand (Aerated)	IOCS (Aerated)
60	0 10	0.01	0.01	0 00	0 28	0 16	0 10	0 04
120	0.05	0.02	0.01	0.00	0.2	0.01	0 10	0 02
240	0.04	0 01	0 04	0 00	0 16	0 04	0.14	0 01
360	0.04	0.01	0 05	0 00	0 15	0.09	0 16	0 01
600	0.04	0.01	0.08	0 00	0 49	0 11	0 16	0 03
1200	0 03	0.01	0.42	0.03	0 72	0 14	0 20	0 08
1440	0.04	0.02	0 71	0.06	1.37	0.16	0 22	0 17

Detailed column tests were conducted with settled and aerated neutralisation tank effluent to study the effect of some relevant engineering parameters

5.2 Detailed Column Tests

Detailed column tests (column ID 2 54 cm, IOCS depth 45 cm, EBCT 9.3 and 15.5 min) were conducted to study the effect of bed contact time and aeration on the removal of copper and zinc from the neutralisation tank effluent (Fig 8). The tests further substantiated the need for aeration of the settled neutralisation tank effluent, as in the column runs using the nonaerated effluent there was much earlier breakthrough for both coper (50 bed volumes) and zinc (10 bed volumes) than in the column runs using the aerated effluent, copper (110 bed volumes) and zinc (35 bed volumes) Also, the effluent copper and zinc concentrations after the breakthrough were much higher for the nonaerated effluent (copper 1.0 mg Cu/L and zinc 5.2 mg Zn/L after 150 bed volumes) than for the aerated effluent (copper 0.015 mg Cu/L and zinc 3 2 mg Zn/L after 150 bed volumes). Increasing the empty bed contact time (EBCT) from 9.3 min to 15.5 min resulted in even better performance — breakthrough was further delayed (for copper, from 110 to 150 bed volumes and for zinc, from 35 to 70 bed volumes) and the effluent metal concentrations after breakthrough were even lower (copper less than 0.02 mg Cu/L and zinc less than 2.1 mg Zn/L up to 200 bed volumes). Based on these results, it is recommended that for use of IOCS treatment as a polishing unit for the existing wastewater treatment at the LML, Kanpur, aeration of the settled neutralisation tank effluent is a must and the empty bed contact time be about 15 min for better performance

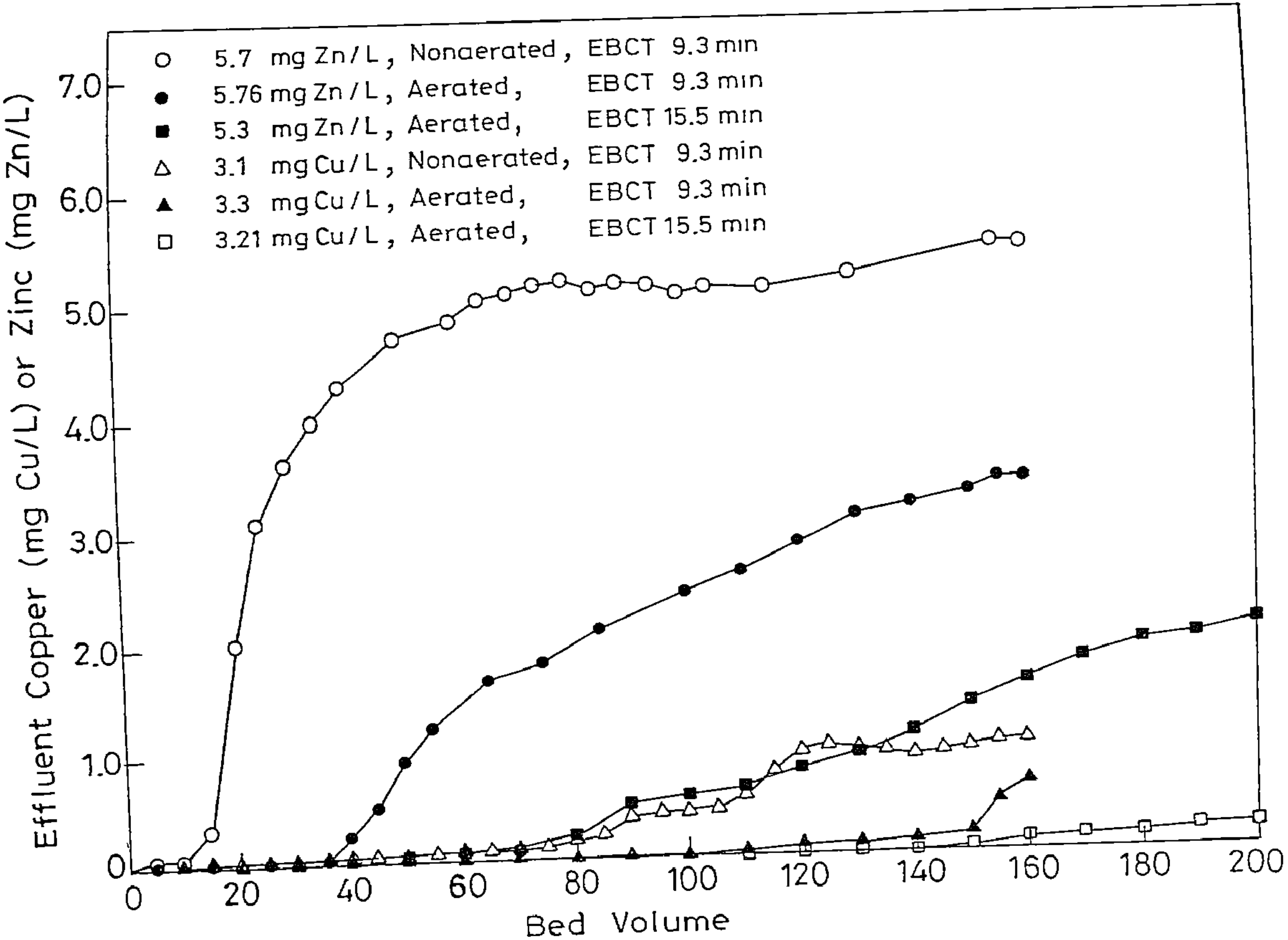

Fig. 8 Effect of bed contact time and aeration on removal of copper and zinc from neutralisation tank effluent by IOCS in detailed column tests.

5.3 Loading-Regeneration Study

Detailed column test was employed to study the effect of successive loading-regeneration on the performance of IOCS in removing copper and zinc from the aerated neutralisation tank effluent. A hydraulic loading rate of 0.108 m^3/m^3 min (EBCT 9 3 min) was used and column runs were for a throughput of 150 bed volumes. Following termination of a run, the IOCS medium was regenerated *in situ* — backwashing (40% bed expansion) with 2.5 L of tap water followed by regeneration with 2 0 L of a 0 03 M $NaNO_3$ solution adjusted to pH 2.0 with nitric acid. The column was then equilibriated by circulating 2 5 L of a 0 03 M $NaNO_3$ solution adjusted to the pH of the wastewater Both the backwash water and the regenerant were collected for five successive cycles of operation and analysed for copper and zinc Using the data, a loading-regeneration material balance was made in terms of the metal on IOCS subjected to regeneration (metal picked up in loading cycle in addition to that remaining from the preceding cycle) and the metal recovered in regeneration.

Performance of the IOCS in terms of copper removal was excellent and effluent copper in all five cycles remained below 0.1 mg Cu/L throughout (Fig 9). For zinc, however, effluent levels were high but remained below 3 mg Zn/L in all cycles (Fig 9) Edwards and Benjamin (1989b) reported lower affinity of Zn for the iron oxide coating. Benjamin et al. (1996) reported earlier breakthrough and highest effluent level of zinc among several metals (zinc, cadmium, nickel and copper) in treating a simulated fly ash leachate by IOCS. According to the loading-regeneration material balance (Table 3), good metal recovery in case of both copper (81.26% - 92.89%) and zinc (76.13%

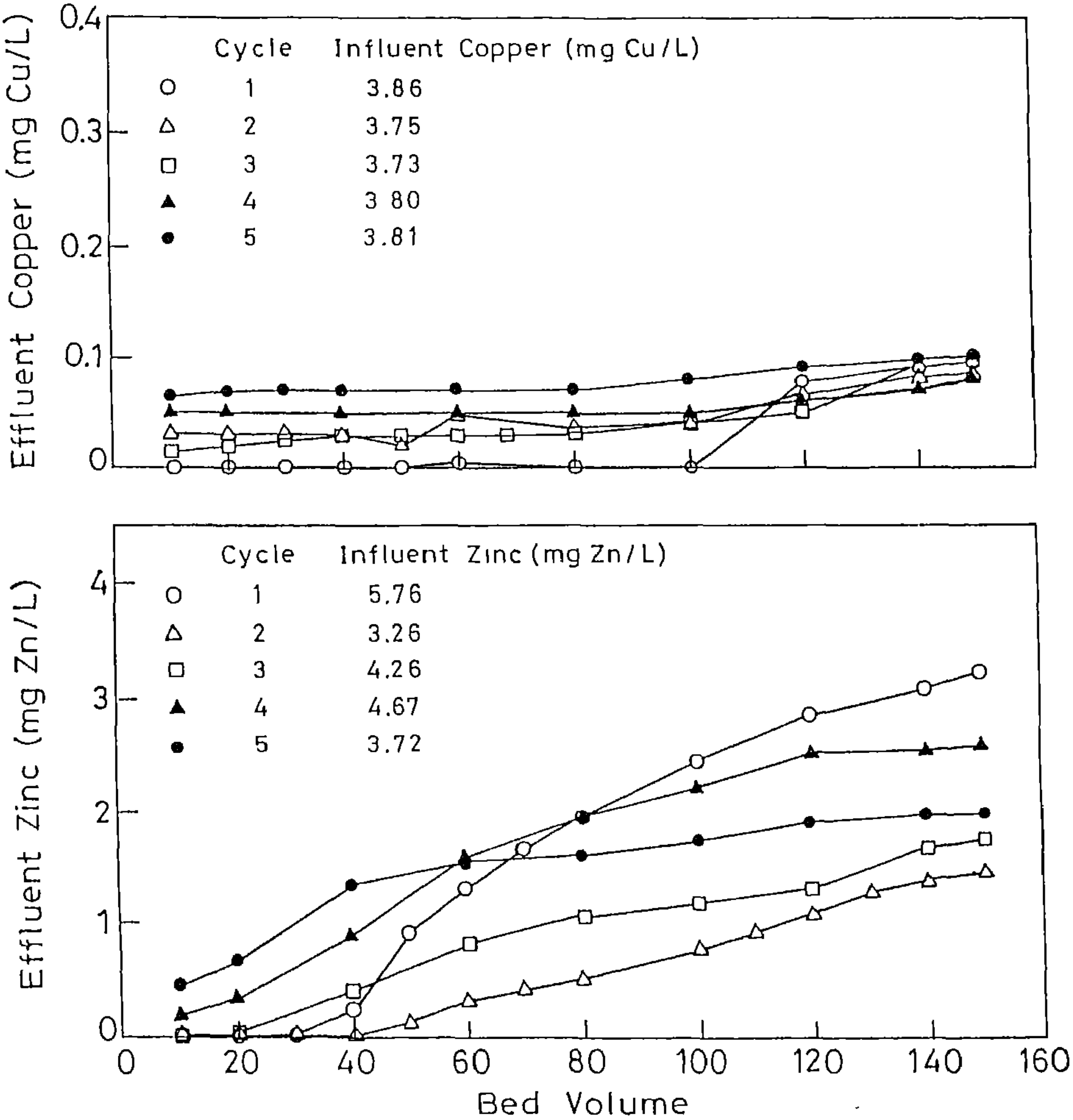

Fig. 9 Performance of IOCS in removal of copper and zinc from aerated neutralisation tank effluent in five successive loading-regeneration cycles.

Table 3 : Loading-regeneration material balance.

	Cycles									
	1		2		3		4		5	
	Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc	Copper	Zinc
Metal from preceding cycle ($\mu g/g$)	0	0	31.92	51.38	28.56	55.72	41.80	76.16	61.32	82.16
Metal picked up in loading cycle ($\mu g/g$)	423.38	448.02	370.12	288.23	384.01	324.88	390.0	302.06	388.56	226.47
Total metal on IOCS subjected to regeneration ($\mu g/g$)	423.38	448.02	402.04	339.61	412.57	380.60	431.80	378.23	449.88	308.62
Metal recovered in regeneration ($\mu g/g$)	391.47	396.65	373.47	283.89	370.78	304.43	370.48	296.08	365.57	234.94
Metal remaining on IOCS ($\mu g/g$)	31.92	51.38	28.56	55.72	41.80	76.17	61.32	82.16	84.31	73.68
Recovery of metal (%)	92.46	88.53	92.89	83.59	89.87	79.99	85.79	78.28	81.26	76.13

- 88 53%) was observed

5.4 Concluding Remarks

The study established the usefulness of IOCS treatment as a polishing unit for the existing wastewater treatment to further improve the effluent quality of the metal-plating wastewater at the LML, Kanpur. However, optimisation of the process in terms of aeration (pressure and duration), hydraulic loading rate and IOCS depth for copper and zinc removal, as well as regeneration procedure (regenerant, pH and duration) for copper and zinc recovery needs to be addressed in more detail

6 SUMMARY

The present study was undertaken to assess the suitability of a novel method, adsorptive filtration by iron oxide-coated sand (IOCS), for treatment of metal-plating wastewaters from an automobile industry — copper-plating and zinc-plating wastewaters from the Lohia Machines Limited (LML), Kanpur. The study included investigation on the suitability/usefulness of three methods of iron oxide coating Coating with ferric nitrate and sodium hydroxide together produced the best IOCS in terms of iron oxide content, longevity and durability, and metal removal. Preliminary tests and practical considerations indicated that one-step treatment of the wastewaters using IOCS was not feasible, but the process appeared promising as a polishing unit for the existing wastewater treatment (alkaline chlorination followed by neutralisation and settling) to improve the effluent quality. Batch sorption and preliminary column tests showed good removal of copper and zinc from the aerated neutralisation tank effluent.

Detailed column tests showed excellent removal of copper and zinc up to 110 and 150, and 35 and 70 bed volumes for empty bed contact time of 9 3 and 15.5 min, respectively from the aerated neutralisation tank effluent Five cycles of detailed column tests, using a hydraulic loading rate of 0.108 m^3/m^3 min (EBCT 9.3) including regeneration by 0.03M $NaNO_3$ at pH 2.0, further indicated suitability of IOCS in the removal and recovery of copper and zinc. However, optimisation of the process in terms of aeration requirements (pressure and duration), hydraulic loading rate and IOCS depth for copper and zinc removal as well as the regeneration procedure (regenerant, pH and duration) for copper and zinc recovery need to be addressed in more detail.

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